

## Supporting information

### Antioxidant Redox Sensors Based on DNA Modified Carbon Screen Printed Electrode

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#### S.1 Chemicals and materials

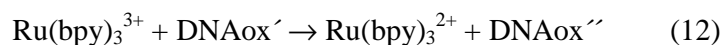
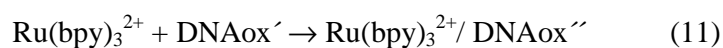
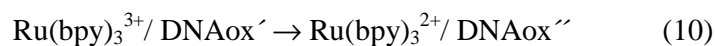
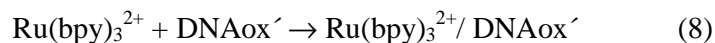
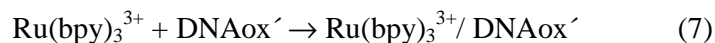
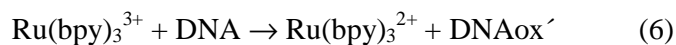
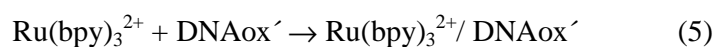
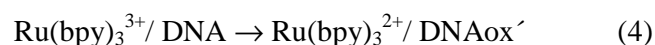
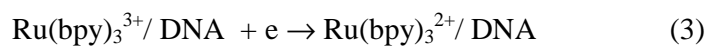
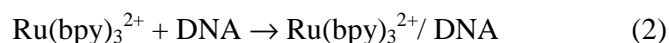
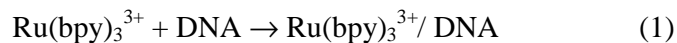
Salmon testes DNA sodium salt (Sigma) and  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (Aldrich) were dissolved in water used as stock solution at concentrations of 5 mM (nucleotide phosphate concentration) and 1 mM, respectively. The PBS buffer was made of sodium phosphate ( $\text{Na}_2\text{HPO}_4$ :  $\text{NaH}_2\text{PO}_4$  = 81:19, molar ratio) and NaCl dissolved in water at a final concentration of 50 and 10 mM, respectively (pH 7.4). Screen printed electrodes (SPEs, 12.5 mm<sup>2</sup>) were used as working electrodes. An Ag/AgCl/saturated KCl reference electrode and a platinum counter electrode were used.

#### S.2 Simulations

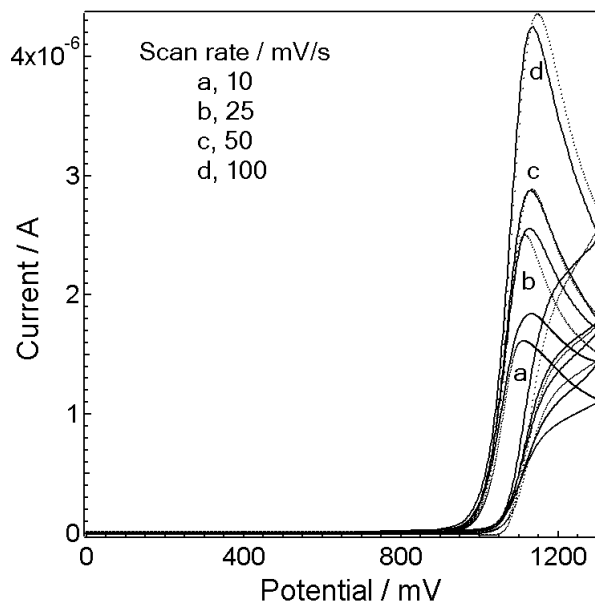
PGSTAT 30 potentiostat was used for electrochemical study. Cyclic voltammograms were simulated using the DigiSim 3.03 software (BAS Inc.). Equations 1 to 12 from the scheme illustrated below [1] were used for simulation when  $\text{Ru}(\text{bpy})_3^{3+/2+}$  is bound to DNA. The forward rate constants for all binding steps were assumed to be diffusion limited and were fixed at  $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The default transfer coefficient ( $\alpha$ ) is 0.5. For simulations that returned homogeneous guanine-metal electron-transfer rate constants, the input DNA nucleotide phosphate concentrations was in terms of guanine concentration, and here we assume that salmon testes DNA is 25% guanine. Second order guanine oxidation rate constants were determined by fitting of cyclic

voltammetric data using the listed mechanisms.

At lower salt concentrations (50 mM NaCl plus 10 mM sodium phosphate, pH 7.4), the electrostatic binding of  $\text{Ru}(\text{bpy})_3^{3+/2+}$  to the DNA becomes important and digital simulation requires more extensive mechanisms to fit the data. We use equations 1 to 12 to describe the mechanism under this condition.



Simulation results under low salt conditions are shown in Fig. S.1. For these simulations, the best fit for scan rate  $50 \text{ mV s}^{-1}$  was obtained, and the second order rate constant for DNA oxidation (equation 6) obtained by simulation is  $1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .



**Fig. S.1.** Cyclic voltammograms (solid line) and digital simulations (dot line) using equations 1 to 12 for  $5.0 \times 10^{-5}$  M  $\text{Ru}(\text{bpy})_3^{2+}$  plus 1.25 mM salmon testes DNA in 50 mM NaCl and 10 mM sodium phosphate, pH 7.4, area (planar) =  $12.5 \text{ mm}^2$ ,  $E^\circ$  (bound) 1.07 V,  $k_s(\text{free})$  and  $k_s(\text{bound}) = 0.02 \text{ cm/s}$ ,  $\alpha$  (free) and  $\alpha$  (bound) = 0.5,  $K_{\text{Ru}(\text{bpy})_3^{2+}} = 2000 \text{ M}^{-1}$ ,  $K_{\text{Ru}(\text{bpy})_3^{3+}} = 10^4 \text{ M}^{-1}$ ,  $k_f(1) = k_f(2) = k_f'(7) = k_f'(8) = k_f''(11) = 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , [guanine] =  $3.1 \times 10^{-4} \text{ M}$ ,  $D_{\text{Ru}(\text{bpy})_3^{2+}} = D_{\text{Ru}(\text{bpy})_3^{3+}} = 1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $D_{\text{DNA}}(\text{all forms}) = 5.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ .  $k_4 = 10 \text{ s}^{-1}$ ,  $k_{10} = 0.75 \text{ s}^{-1}$ ,  $k_6 = 1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{12} = 200 \text{ M}^{-1} \text{ s}^{-1}$ .

## Reference

[1] Johnston, D. H.; Thorp, H. H. *J. Phys. Chem.* **1996**, *100*, 13837